RESEARCH   **Open Access**

Process optimization studies of Congo red dye adsorption onto cashew nut shell using response surface methodology

Senthil Kumar Ponnusamy[1*] and Ramalingam Subramaniam[2*]

Abstract

Background: High cost of commercially available activated carbon increases the treatment cost. Hence, no-cost or low-cost, alternate adsorbents are the current thirst in this area of research. The limitations of conventional methods of experimentation can mislead the optimum operating conditions. The present investigation mainly deals with utilization of the low-cost, agricultural waste adsorbent, cashew nut shell, and the determination of the optimum conditions for Congo red dye removal from an aqueous solution using response surface central composite design methodology.

Results: The adsorbent, cashew nut shell, can remove the Congo red dye completely from the aqueous solution. The parameters pH, adsorbent dose, initial dye concentration, time, and temperature considered for this investigation play an important role in the adsorption studies of Congo red dye removal. The optimum values of pH, adsorbent dose, initial dye concentration, time, and temperature were found to be 3.2, 24.76 g/L, 20 mg/L, 67 min, and 30°C for complete removal of Congo red dye, respectively. The experimental values were in good agreement with predicted values.

Conclusions: Adsorption of Congo red dye from an aqueous solution with a low-cost adsorbent prepared from an agricultural waste was studied to determine the potential use of this adsorbent for complete removal of the dye. Batch studies were performed to address the influence of various parameters such as pH, adsorbent dose, initial dye concentration, time, and temperature. Response surface central composite design methodology was used to find the interaction among the variables and to determine the optimum conditions towards the adsorption of dye from the aqueous solution. The optimum values of pH, adsorbent dose, initial dye concentration, time, and temperature were found to be 3.2, 24.76 g/L, 20 mg/L, 67 min, and 30°C for complete removal of Congo red dye, respectively. The experimental values were in good agreement with predicted values.

Keywords: Cashew nut shell, Congo red dye, Response surface methodology, Statistical analysis, Optimization

Background

The dye effluents are considered to be highly toxic to the aquatic species and are found to affect the symbiotic process by disturbing the natural equilibrium by reducing photosynthetic activity and primary production due to the colorization of the water [1]. Removal of these dyes from effluents in an economic way remains as a major problem for textile industries [2,3]. The most commonly used methods for color removal are biological and chemical precipitation. However, these processes are effective and economic only in cases where solute concentrations are relatively high [4]. Even though many methods were explored to address this environmental and economic concern, there are advantages and disadvantages in each and every method used for dye removal from wastewaters [5]. Many physicochemical methods have been tested, but adsorption is considered to be superior to other techniques. This is attributed to its low cost, easy availability, simplicity of design, high efficiency, easy operation, biodegradability, and ability to treat dyes in more concentrated forms [6,7]. The adsorption technique has been proven to be an excellent way to treat effluents,

* Correspondence: senthilchem8582@gmail.com; raams@louisiana.edu
[1]Department of Chemical Engineering, SSN College of Engineering, Chennai 603 110, India
Full list of author information is available at the end of the article

offering advantages over conventional processes, especially from the environmental point of view [2]. Weber and Morris [2] have identified many advantages of adsorption over several other conventional treatment methods. The adsorption of dyes on various types of materials has been studied in detail. Those include the following: activated carbon [8], peat [9], chitin [10], silica [11], hardwood [12], hardwood sawdust [13], bagasse pith [14], fly ash [15,16], mixture of fly ash and coal [17], chitosan fiber [18], paddy straw [19], rice husk [20], slag [21], chitosan [22], acid-treated spent bleaching earth [23], palm fruit bunch [24], and bone char [25]. Adsorption with activated carbon has been used widely for the removal of dyes from wastewater [26-31]. Activated carbon was being used as a potential adsorbent because of its high efficiency [32]. Commercially available activated carbons are usually derived from natural materials such as wood or coal which are expensive [33,34]. Increase in the price of activated carbon results in increased treatment cost for the developing countries like India. Hence, no-cost or low-cost, alternate adsorbents with equivalent capabilities of activated carbon are the current thirst in this area of research. Consequently, low-cost activated carbons from agricultural solid wastes are being investigated for a long time.

The conventional method of studying a process by changing one variable at a time and keeping the other variables at a constant level does not depict the combined effect of all the factors involved. Moreover, this method is time-consuming and also requires a large number of experiments to determine optimum levels, which may or may not be reliable. These limitations of the conventional method can be eliminated by simultaneously varying all the affecting parameters by using a statistical experimental design such as the response surface methodology (RSM) [35]. RSM, initially described by Box and Wilson [36], is an experimental approach to identify the optimum conditions for a multivariable system. RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes that can be used to evaluate the relative significance of all the factors involved in the process even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or the process [37]. The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, and reduced development time and overall costs [38].

The main objectives of the present investigation are the utilization of the low-cost, agricultural waste adsorbent, cashew nut shell (CNS), and the determination of the optimum conditions for Congo red (CR) dye removal from an aqueous solution using response surface central composite design methodology. In this study, the central composite design was selected to determine the effect of experimental parameters and their interactions over the removal of CR. The interactions between factors that influence the percentage of CR removal were established. The optimum value of the parameters was also determined for removal of CR from the aqueous solution using RSM.

Methods

Cashew nut shells collected from Pudukkottai District, Tamilnadu, India were used as an adsorbent. This natural waste was thoroughly rinsed with water to remove dust and the soluble material and was allowed to dry at room temperature. The dried natural waste was crushed into powder and sieved through the sieves. CNS particles with a mesh size of 200 to 30 were taken for the adsorption studies. The proximate and ultimate analysis of cashew nut shells are shown in Table 1. The specific surface area and the pore structure of the CNS were determined by using a surface area and pore size analyzer (Autosorb-I, Quantachrome Instruments, Boynton Beach, FL, USA) on nitrogen adsorption at 77 K. The specific surface area was calculated using the BET equation [39]. It was found that the BET surface area, pore volume, average pore diameter, and bulk density of the CNS were 395 m^2/g, 0.4732 cm^3/g, 5.89 nm, and 0.415 g/cm^3, respectively.

Congo red (CI = 22120) was supplied by Merck (Mumbai, India). A stock solution of CR dye was prepared (100 mg/L) by dissolving a required amount of dye powder in deionized water. The stock solution was diluted with deionized water to obtain the desired concentration ranging from 20 to 100 mg/L.

The concentration of CR in the experimental solution was determined from the calibration curve prepared by measuring the absorbance of different known concentrations of CR solutions at λ_{max} = 497 nm using a UV–vis spectrophotometer (Shimadzu, Kyoto, Japan). The pH of the solution was measured with a Hanna pH meter using a combined glass electrode (model HI 9025C, Hanna Instruments, Singapore).

Adsorption experiments were conducted as per the design developed with response surface central composite design methodology. The experiments were carried out in 250-mL Erlenmeyer flasks with the working volume of 100 mL of reaction mixture. The initial pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. The flasks were shaken for the specified time period in a rotary shaker. The flasks were withdrawn from the shaker after the desired time of reaction. The residual dye concentration in the reaction mixture was analyzed by centrifuging (5,000 rpm, R-24 REMI Centrifuge, Mumbai, India) the reaction mixture and then measuring the absorbance of the supernatant at the wavelength that corresponds to the maximum absorbance of the sample. Dye concentration in the reaction mixture was calculated

Table 1 Properties of the cashew nut shells

Proximate analysis (wt.%)		Ultimate analysis (wt.%)		Ash chemical composition (wt.%)	
Volatile matter	65.21	Carbon	45.21	Silica	64.53
Moisture	9.83	Hydrogen	4.25	Iron oxide	3.27
Ash	2.75	Oxygen	37.75	Aluminum oxide	2.19
Fixed carbon	22.21	Nitrogen	0.21	Calcium oxide	26.89
		Sulfur	Nil	Magnesium oxide	2.49
		Moisture	9.83	Sodium oxide	0.63
		Ash	2.75		

from the calibration curve. The $\lambda_{\max}$ values of the wastewater samples varied by ±10 nm from the $\lambda_{\max}$ values of pure samples. Each determination is repeated three times, and the results given were their average value. The percentage of CR removal was taken as a response (Y) of the experimental design and calculated as follows:

$$\% \text{ CR dye removal} = \left(\frac{C_i - C_f}{C_i}\right) \times 100, \qquad (1)$$

where C_i is the initial concentration of dye in the solution and C_f is the final concentration of dye in the solution.

The pH, adsorbent dose, initial dye concentration, time and temperature are chosen as the independent input variables and the efficiency of dye removal as dependent response variable. Independent variables, experimental range and levels for congo red dye removal are given in Table 2. A 2^5 full factorial experimental design [36], with ten replicates at the center point, 10 experiments at axial points and thus a total of 52 experiments are employed in this study. The alpha value is chosen as face centered ($\alpha = 1$). When $\alpha = 1$, the axial points are placed on the 'cube' portion of the design. This is an appropriate choice when the cube points of the design are at the operational limits. The center point replicates are chosen to verify any change in the estimation procedure, as a measure of precision property. The experimental plan showing the coded value and uncoded value of the variables together with the dye

Table 2 Experimental range and levels of independent process variables

Independent variable	Range and level		
	−1	0	+1
pH (X_1)	2	6	10
Adsorbent dose (X_2, g/L)	5	17.5	30
Initial dye concentration (X_3, mg/L)	20	60	100
Time (X_4, min)	0	60	120
Temperature (X_5, °C)	30	45	60

removal efficiency for CR is given in Table 3. For statistical calculations, the variables X_i are coded as x_i according to the following relationship:

$$x_i = \left(\frac{X_i - X_0}{\delta_X}\right), \qquad (2)$$

where x_i is the dimensionless coded value of the variable X_i, X_0 is the value of the X_i at the center point, and δ_X is the step change.

The behavior of the system is explained by the following quadratic equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (3)$$

where β_0 is the offset term, β_i is the linear effect, β_{ii} is the squared effect, β_{ij} is the interaction effect, and x_i is the dimensionless coded value of the variable X_i.

The results of the experimental design are studied and interpreted by MINITAB 14 (State College, PA, USA) statistical software to estimate the response of the dependent variable.

Results and discussion

The experiments were performed at the specified combinations of the physical parameters using statistically designed experiments in order to study the combined effects of these factors. The main effects of all the variables taken into consideration in this work are presented in Figure 1. From the figure, it is clear that the variables considered for this investigation play an important role in the adsorption studies of CR dye removal since each variable has a significant contribution on the percentage of dye removal. A main effect occurs when the mean response changes across the levels of a factor. The main effect plots were used to plot data means when multiple factors are involved in the system/process and also to compare magnitudes of marginal means. The points in the plot were the means of the response variables at the various levels of each factor, with a reference line drawn at the grand mean of the response data. Grand mean is the mean of all observations, as opposed to the mean of

Table 3 Central composite design matrix with experimental and predicted values

Coded values					Uncoded values					% Removal	
pH	Adsorbent dose (g/L)	Initial concentration (mg/L)	Time (min)	Temperature (°C)	pH	Adsorbent dose (g/L)	Initial concentration (mg/L)	Time (min)	Temperature (°C)	Experimental	Predicted
−1	1	1	−1	−1	2	30	100	0	30	0	−0.05
−1	−1	1	−1	1	2	5	100	0	60	0	0.04
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
1	1	1	−1	−1	10	30	100	0	30	0	−0.34
−1	−1	−1	1	−1	2	5	20	120	30	62.33	62.35
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
−1	−1	−1	1	1	2	5	20	120	60	57.57	57.88
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
−1	1	1	1	1	2	30	100	120	60	79.34	79.45
1	1	1	−1	1	10	30	100	0	60	0	−0.05
−1	1	−1	−1	−1	2	30	20	0	30	0	0.03
−1	1	−1	1	−1	2	30	20	120	30	98.52	98.45
1	−1	1	−1	−1	10	5	100	0	30	0	−0.01
1	−1	−1	1	−1	10	5	20	120	30	52.89	53.02
1	−1	−1	−1	1	10	5	20	0	60	0	−0.03
1	−1	1	1	−1	10	5	100	120	30	38.54	38.53
1	1	1	1	1	10	30	100	120	60	70.34	70.34
0	1	0	0	0	6	30	60	60	45	86.04	86.43
0	0	0	0	−1	6	17.5	60	60	30	82.08	82.33
0	0	0	0	0	6	17.5	60	60	45	81.06	80.99
−1	1	−1	−1	1	2	30	20	0	60	0	−0.02
1	1	1	1	−1	10	30	100	120	30	73.93	74.23
−1	1	−1	1	1	2	30	20	120	60	94.24	94.22
0	−1	0	0	0	6	5	60	60	45	68.31	68.43
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
−1	−1	1	1	−1	2	5	100	120	30	48.56	48.15
−1	0	0	0	0	2	17.5	60	60	45	81.67	81.94
0	0	1	0	0	6	17.5	100	60	45	81.39	81.66
1	1	−1	1	1	10	30	20	120	60	85.82	85.40
0	0	0	1	0	6	17.5	60	120	45	66.43	66.67
1	0	0	0	0	10	17.5	60	60	45	77.08	77.33

Table 3 Central composite design matrix with experimental and predicted values *(Continued)*

|											
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
1	−1	−1	−1	−1	10	5	20	0	30	0	−0.14
1	−1	−1	1	1	10	5	20	120	60	48.94	48.96
−1	−1	−1	−1	−1	2	5	20	0	30	0	−0.03
−1	−1	−1	−1	1	2	5	20	0	60	0	−0.33
1	1	−1	1	−1	10	30	20	120	30	89.29	89.22
−1	−1	1	−1	−1	2	5	100	0	30	0	0.39
−1	−1	1	1	1	2	5	100	120	60	43.68	43.62
0	0	−1	0	0	6	17.5	20	60	45	88.74	88.98
1	−1	1	−1	1	10	5	100	0	60	0	0.04
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
−1	1	1	−1	1	2	30	100	0	60	0	−0.16
0	0	0	−1	0	6	17.5	60	0	45	0	0.28
1	1	−1	−1	1	10	30	20	0	60	0	0.38
−1	1	1	1	−1	2	30	100	120	30	83.75	83.74
1	−1	1	1	1	10	5	100	120	60	34.47	34.41
0	0	0	0	1	6	17.5	60	60	60	79.98	80.24
0	0	0	0	0	6	17.5	60	60	45	81.21	80.99
1	1	−1	−1	−1	10	30	20	0	30	0	0.02
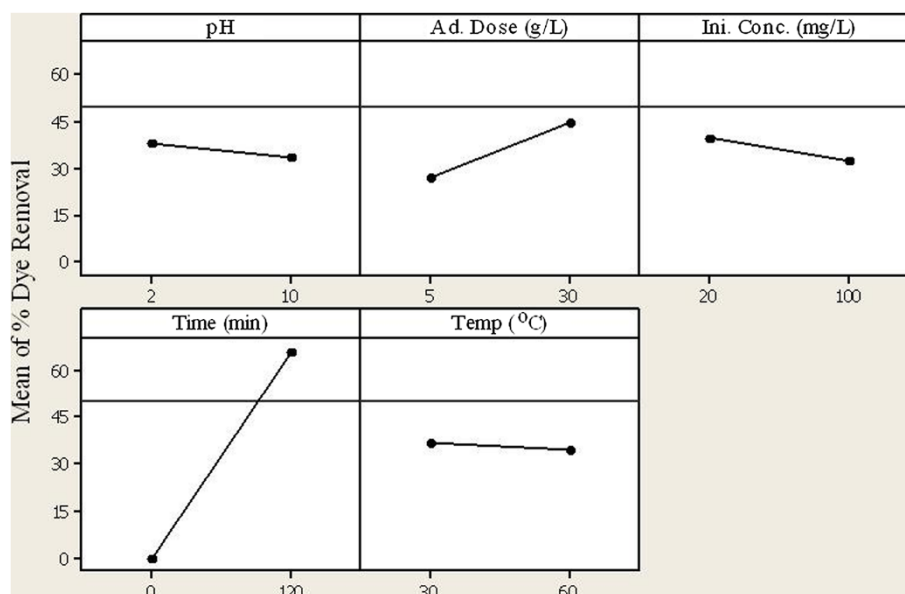
Figure 1 Main effect plot of parameters on CR dye removal.

individual variables. The line drawn across the plot (center line) represents the grand mean. From Figure 1, it is clear that the grand mean of the response falls at around 50% dye removal. Out of the variable considered, adsorbent dose and time are the dominant factors for the percentage of dye removal when compared to other variables.

The percentage of CR dye removal decreases with an increase in initial pH of the system due to its influence on the surface properties of the CNS and ionization/dissociation of the CR molecule. At higher pH, the grand mean drops down to 30%. The maximum removal of dye can be obtained at a low pH. Low pH leads to an increase in H$^+$ ion concentration in the system, and the surface of the CNS acquires a positive charge by absorbing H$^+$ ions. As the CNS surface is positively charged at low pH, a significantly strong electrostatic attraction appears between the positively charged CNS surface and anionic dye molecule, leading to maximum adsorption of dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the CNS does not favor the adsorption of anionic dye molecules due to the electrostatic repulsion. Furthermore, lower adsorption of the CR dye in alkaline medium is also due the competition from excess OH$^-$ ions with the anionic dye molecule for the adsorption sites.

The percentage of CR dye removal is increased with an increase in adsorbent dose. At higher CNS-to-CR concentration ratios, a very fast superficial sorption onto the CNS surface occurs which produces a lower CR concentration in the solution than when the CNS-to-CR concentration ratio is lower. This is because a fixed dose of CNS can

only adsorb a certain amount of dye. Therefore, with higher adsorbent dosage, a larger volume of effluent can be purified with a fixed dosage of CNS. The decrease in the amount of CR adsorbed on to an adsorbent q_e (mg/g) with increasing CNS dose is due to the split in the flux or the concentration gradient between the CR concentration in the solution and the CR concentration in the surface of the CNS. Thus, with increasing CNS dose, the amount of dye adsorbed onto the unit weight of CNS gets reduced, thereby causing a decrease in the q_e value.

The effect of initial dye concentration on adsorption shows that the percentage of CR dye removal decreases with an increase in the initial concentration of CR dye. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of CR between the aqueous phase and the solid phase. The increase in an initial dye concentration also enhances the interaction between CR and CNS. Therefore, an increase in an initial concentration of CR enhances the adsorption uptake of CR. This is due to an increase in the driving force of the concentration gradient, as an increase in the initial dye concentration.

The effect of contact time on the percentage of CR dye removal increases rapidly with time. This indicates that a longer contact time favors the reaction towards the equilibrium between the dye and adsorbent. It may be due to the fact that the available CR dye molecules are preferentially adsorbed to the most active sites of the CNS. The short contact time between the CNS and CR dye molecules gives the less percentage of CR dye removal and equilibrium adsorption capacity and vice versa. The adsorption of CR dye onto the CNS was investigated as a

function of temperature, and the maximum removal of CR dye was obtained at lower temperature. This is mainly due to the decrease in the surface activity, suggesting that adsorption between CR and CNS was an exothermic process.

Response surface methodology has been successfully applied for optimizing conditions for CR dye removal. The experimental results are analyzed through RSM to obtain an empirical model for the best response. The uncoded regression model equation (second-order polynomial) relating the removal efficiency and process parameters is developed and given in Equation 4. The mathematical expressions of the relationship between the independent variables and dependent response are given in terms of uncoded factors. Apart from the linear effect of the parameter for the dye removal, the RSM also gives an insight into the quadratic and interaction effect of the parameters. These analyses are done by means of Fisher's F test and Student's t test. Student's t test was used to determine the significance of the regression coefficients of the parameters. The P values are used as a tool to check the significance of each of the interaction among the variables, which in turn may indicate the patterns of the interactions among the variables. In general, the larger the magnitude of t and smaller the value of P, the more significant is the corresponding coefficient term [40]. The regression

coefficient and the t and P values for all the linear, quadratic, and interaction effects of the parameters are given in Table 4. From the high t values and very small P values, it is observed that the coefficients for the linear effect and quadratic effect of all the factors are highly significant. The high P values of 0.593, 0.224, and 0.752 for the interaction effect of pH and adsorbent dose, adsorbent dose and temperature, and initial concentration and temperature did not seem to be significant, respectively. The response surface plots to estimate the removal efficiency over independent variables are shown in Figure 2. The peak of the surface plot shows an optimum value of the percentage of dye removal for the relative effects of variable pH and adsorbent dose (Figure 2a), adsorbent dose and temperature (Figure 2b), initial concentration and time (Figure 2c), and initial concentration and temperature (Figure 2d) by keeping the other three variables at the midpoint values. From Figure 2, it is clear that the interaction effects of adsorbent dose-pH, adsorbent dose-temperature, and initial concentration-temperature are not significant towards the percentage of dye removal. The response surfaces of mutual interactions between the variables other than those discussed above are found to be elliptical which explains the significance of those variables. The significance of these interaction effects between the variables would have been lost if the

Table 4 Estimated regression coefficients and corresponding *t* and *P* values

| Term	Coefficient	SE coefficient	t	P
Constant	2.92257	1.35459	2.158	0.039
pH	0.96179	0.13781	6.979	0
Adsorbent dose (g/L)	0.79432	0.04156	19.112	0
Initial concentration (mg/L)	−0.31653	0.01378	−22.969	0
Time (min)	2.12829	0.00661	321.876	0
Temperature (°C)	−0.13244	0.06976	−1.899	0.067
pH*pH	−0.08497	0.0108	−7.866	0
Adsorbent dose (g/L)*Adsorbent dose (g/L)	−0.02278	0.00111	−20.594	0
Initial concentration (mg/L)*Initial concentration (mg/L)	0.00271	0.00011	25.056	0
Time (min)*Time (min)	−0.0132	0.00005	−274.939	0
Temperature (°C)*Temperature (°C)	0.00131	0.00077	1.71	0.097
pH*Adsorbent dose (g/L)	0.00052	0.00096	0.54	0.593
pH*Initial concentration (mg/L)	−0.00046	0.0003	−1.515	0.14
pH*Time (min)	−0.00961	0.0002	−47.954	0
pH*Temperature (°C)	0.00169	0.0008	2.113	0.043
Adsorbent dose (g/L)*Initial concentration (mg/L)	−0.00025	0.0001	−2.62	0.014
Adsorbent dose (g/L)*Time (min)	0.01201	0.00006	187.376	0
Adsorbent dose (g/L)*Temperature (°C)	0.00032	0.00026	1.242	0.224
Initial concentration (mg/L)*Time (min)	−0.00152	0.00002	−76.049	0
Initial concentration (mg/L)*Temperature (°C)	−0.00003	0.00008	−0.319	0.752
Time (min)*Temperature (°C)	−0.00116	0.00005	−21.718	0
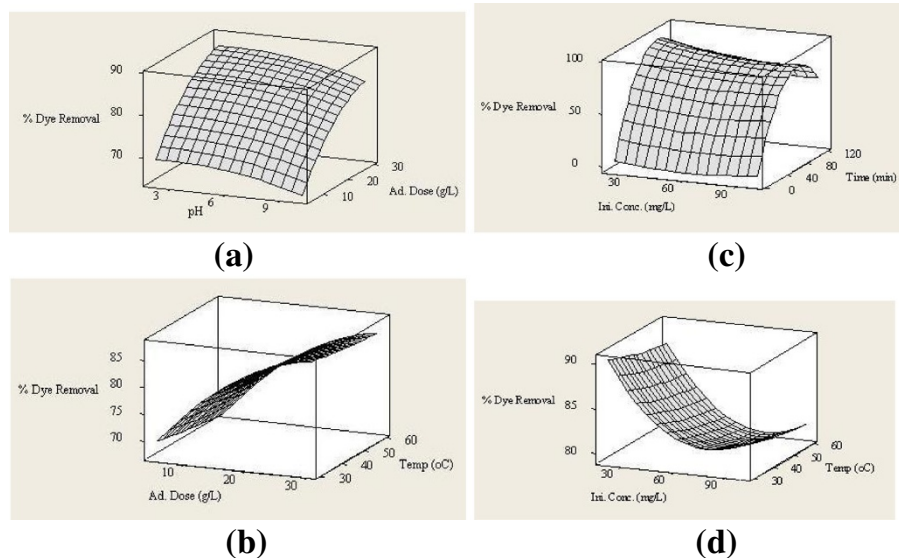
Figure 2 Response surface plot of CR dye removal. (**a**) pH and adsorbent dose, (**b**) adsorbent dose and temperature, (**c**) initial concentration and time, and (**d**) initial concentration and temperature.

experiments are carried out by conventional methods. The experimental results and the results of theoretically predicted responses (using the model equation) are shown in Table 3.

$$\begin{aligned}
\eta =\ & (2.9226) + (0.9618\ X_1) + (0.7943\ X_2) \\
& - (0.3165\ X_3) + (2.1283\ X_4) - (0.1324\ X_5) \\
& - (0.0850\ X_1^2) - (0.0228\ X_2^2) + (0.0027\ X_3^2) \\
& - (0.0132\ X_4^2) + (0.0013\ X_5^2) + (0.0005\ X_1\ X_2) \\
& - (0.0005\ X_1\ X_3) - (0.0096\ X_1\ X_4) \\
& + (0.0017\ X_1\ X_5) - (0.0003\ X_2\ X_3) \\
& + (0.012\ X_2\ X_4) + (0.00032\ X_2\ X_5) \\
& - (0.0015\ X_3\ X_4) - (0.00003\ X_3\ X_5) \\
& - (0.0012\ X_4\ X_5),
\end{aligned}$$

(4)

where X_1 is the pH, X_2 is the adsorbent dose (g/L), X_3 is the initial concentration of adsorbate (mg/L), X_4 is the time (min), and X_5 is the temperature (°C).

The statistical significance of the ratio of the mean square variation due to the regression and mean square residual error is tested using analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypothesis on the parameters of the model [41]. According to the ANOVA (Table 5), the F statistic values for all regressions are higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated values of P lower

than 0.01 indicate that the model is statistically significant [42]. The ANOVA table also shows a term for the residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct and has very good agreement with the experimental value. The high value of R^2 and R_{adj}^2 explains that the model is significant.

The $F_{Statistics}$ value of 48,028 is greater than the tabulated $F_{20,31}$ which indicates that the fitted model exhibits a lack of fit of 0.000 at the 99% confidence level. The ANOVA indicates that the second-order polynomial model Equation 4 is highly significant and adequate to represent the actual relationship between the response (percent removal efficiency) and variables, with P values (0.0000) and a high value of the coefficient of determination (99.7%). This implies that 99.7% of the sample variation is explained by the independent

Table 5 ANOVA results for the quadratic model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	20	71037.4	71037.4	3551.87	48028	0
Linear	5	40891.6	11392.6	2278.52	30810	0
Square	5	26915.5	26915.5	5383.09	72790	0
Interaction	10	3230.3	3230.3	323.03	4368	0
Residual error	31	2.3	2.3	0.07		
Lack of fit	22	2.3	2.3	0.1	45.91	0
Pure error	9	0	0	0		
Total	51	71039.7				

$R^2 = 0.997$; $R_{adj}^2 = 0.994$. DF, degrees of freedom; Seq SS, sequential sums of squares; Adj SS, adjusted sums of squares; Adj MS, adjusted mean squares.

variables. Even though the interaction terms pH and adsorbent dose, adsorbent dose and temperature, and initial concentration and temperature are found to be insignificant, the oval model holds good agreement with the experimental data.

The model Equation 4 is optimized using a multistage Monte-Carlo optimization technique [43]. The optimum values of the process parameters are obtained in uncoded units. The optimum values of the process variables for the maximum removal efficiency are 3.2, 24.76 g/L, 20 mg/L, 67 min, and 30°C for the variables pH, adsorbent dose, initial dye concentration, time, and temperature, respectively. The percentage of dye removal at the optimum conditions simulated from the model is 100%. The experiments were done at optimum conditions, and the percentage of dye removal thus obtained is 99.99% which has a very close agreement with the model. These results closely agree with the optimum values obtained from the response surface methodology as 3.2557, 24.7634 g/L, 20 mg/L, 67.1815 min, and 30°C for the variables pH, adsorbent dose, initial dye concentration, time, and temperature, respectively. These results confirm that the RSM could be effectively used to optimize the process parameters in complex processes using the statistical design of experiments.

Experimental

Adsorption experiments were conducted as per the design developed with response surface central composite design methodology. All the experiments were done in duplicate to minimize the experimental error. The results given in Table 3 are the average experimental values. The detailed experimental procedure was discussed in 'Methods' section.

Conclusion

A novel, low-cost adsorbent prepared from agricultural waste, cashew nut shell, is successfully applied for the removal of CR from its aqueous solution. The specific surface area, pore volume, and average pore diameter calculated by the BET equation states the effectiveness of the CNS adsorbent for the removal of CR from aqueous solution. The effect of pH, adsorbent dose, initial dye concentration, time, and temperature on the adsorption was studied with the 52 experiments designed by the 2^5 full factorial central composite designs. This study clearly shows that the response surface methodology is one of the suitable methods to optimize the best operating conditions to maximize the dye removal. The statistical analysis results proved the significance of the model developed from experimental data to optimize the parameters. A significant interaction was observed in CR removal with the combination effects of pH, adsorbent dose, initial dye concentration, time, and temperature.

The optimum values of pH, adsorbent dose, initial dye concentration, time, and temperature were found to be 3.2, 24.76 g/L, 20 mg/L, 67 min, and 30°C for the complete removal of CR dye, respectively. The experimental values were in good agreement with the model predicted values.

Authors' contributions
SP carried out the adsorbent preparation, characterization, and experimentation and wrote the methods and experimental sections. RS carried out the experimental design, data analysis, optimization, and manuscript writing. Both authors read and approved the final manuscript.

Authors' information
RS is working in the Department of Chemical Engineering, University of Louisiana at Lafayette, Lafayette, USA. His areas of research are environmental engineering, bio processing, renewable energy, and process modeling and simulation. SP is working in the Department of Chemical Engineering, SSN College of Engineering Chennai, India. Currently, he is doing research in the fields of waste water treatment and chemical reaction engineering.

Author details
[1]Department of Chemical Engineering, SSN College of Engineering, Chennai 603 110, India. [2]Department of Chemical Engineering, University of Louisiana at Lafayette, Lafayette, LA 70504, USA.

References
1. Malik A, Taneja U (1994) Utilizing fly ash for color removal of dye effluents. Am Dyestuff Rep 83:20–27
2. Weber WJ, Morris JC (1964) Advances in water pollution research. Pergamon Press, New York
3. Arslan I, Balcioglu IA, Bahnemann DW (2000) Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UVA and TiO$_2$/UV-A processes. Dyes Pigments 47:207–218
4. Vadivelan V, Kumar KV (2005) Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J Colloid Interface Sci 286:90–100
5. Garg VK, Amita M, Kumar R, Gupta R (2004) Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. Dyes Pigments 63:243–250
6. Sanghi R, Bhattacharya B (2002) Review on decolorization of aqueous dye solutions by low cost adsorbents. Color Technol 118:256–269
7. Meshko V, Markovska L, Mincheva M, Rodrigues AE (2001) Adsorption of basic dyes on granular activated carbon and natural zeolite. Water Res 35:3357–3366
8. Dedrick RL, Beckmann RB (1967) Kinetics of adsorption by activated carbon from dilute aqueous solution. AIChE J 3:68–75
9. McKay G, Allen SJ, McConvey IF, Otterburn MS (1981) Transport processes in the adsorption of colored ions by peat particles. J Colloid Interface Sci 80:323–339
10. McKay G, Blair HS, Gardner JS (1983) Rate studies for the adsorption of dyestuffs on chitin. J Colloid Interface Sci 95:108–119
11. McKay G (1984) Analytical solution using a pore diffusion model for a pseudo irreversible isotherm for the adsorption of basic dye on silica. AIChE J 30:692–697
12. Asfour HM, Fadeli OA, Nasser MM, El-Geundi MS (1985) Equilibrium studies on adsorption of basic dyes on hardwood. J Chem Technol Biotechnol 35:21–27

13. Asfour HM, Fadeli OA, Nasser MM, El-Geundi MS (1985) Colour removal from textile effluents using hardwood sawdust as adsorbent. J Chem Technol Biotechnol 35:28–35

14. McKay G, Geundi EI, Nasser MM (1987) Equilibrium studies during the removal of dyestuff's from aqueous solutions using bagasse pitch. Water Res 21:1513–1518

15. Khare SK, Panday K, Srivastava RM, Singh VN (1987) Removal of Victoria Blue from aqueous solutions by fly ash. J Chem Technol Biotechnol 38:99–104

16. Gupta GS, Prasad G, Singh VH (1988) Removal of chrome dye from aqueous solutions by fly ash. Water Air Soil Pollut 37:13–24

17. Gupta GS, Prasad G, Singh VH (1990) Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal. Water Res 24:45–50

18. Yoshida H, Fukuda S, Okamota S, Kataoka T (1991) Recovery of direct dye and acid dye by adsorption on chitosan fiber equilibria. Water Sci Technol 23:1667–1676

19. Narmata D, Manzoor A (1993) Dye adsorption by a new low cost material Congo red. Ind J Environ Protec 13:570–576

20. Lee CK, Low KS (1997) Quaternized rice husk as sorbent for reactive dyes. Bioresour Technol 61:121–125

21. Ramakrishna KR, Viraraghavan T (1997) Use of slag for dye removal. Waste Manage 17:483–488

22. Juang RS, Tseng RKL, Wu FC, Lee SH (1997) Adsorption behaviour of reactive dyes from aqueous solution on chitosan. J Chem Technol Biotechnol 70:391–399

23. Lee CK, Low KS (1999) Removal of some organic dyes by acid-treated bleaching earth. Process Biochem 34:451–465

24. Nassar MM (1999) Intraparticle diffusion of basic red and basic yellow dyes on palm fruit bunch. Water Sci Technol 40:133–139

25. Ko DCK, Porter JF, McKay G (2000) Optimized correlations for the fixed bed adsorption of metal ions on bone char. Chem Eng Sci 55:5819–5829

26. Malik PK (2003) Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes Pigments 56:239–249

27. Goyal M, Singh S, Bansal RC (2004) Equilibrium and dynamic adsorption of methylene blue from aqueous solutions by surface modified activated carbon. Carbon Sci 5:170–179

28. Bangash FK, Manaf A (2004) Kinetics of removal of dye (Basic blue 3) from aqueous solution by activated charcoal from the wood of *Braunsonitia papyrilefra* (Paper Mulberry). J Chem Soc Pak 26:111–115

29. Lorenc-Grabowska E, Gryglewicz G (2006) Adsorption characteristics of Congo red on coal-based mesoporous activated carbon. Dyes Pigments 68:1–7

30. Namasivayam C, Kavitha D (2002) Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes Pigments 54:47–58

31. Teng RL, Wu FC, Juang RS (2003) Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons. Carbon 41:487–495

32. Khattri SD, Singh MK (1998) Colour removal from aqueous solutions by adsorption. Ind J Chem Technol 5:230–234

33. Singh BK, Rawat NS (1994) Comparative sorption equilibrium studies of toxic phenols on fly ash and impregnated fly ash. J Chem Technol Biotechnol 61:307–317

34. Hameed BH, Ahmad AL, Latiff KNA (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pig 75:143–149

35. Elibol M (2002) Response surface methodological approach for inclusion of perfluorocarbon in actinorhodin fermentation medium. Process Biochem 38:667–773

36. Box GEP, Wilson KN (1951) On the experimental attainment of optimum conditions. J R Stat Soc Ser B13:1–45

37. Myers RH, Montgomery DC, Anderson-Cook CM (2009) Response surface methodology, process and product optimization using designed experiments 3rd edition. Wiley, Hoboken

38. Annadurai G, Juang RS, Lee DJ (2002) Factorial design analysis of adsorption of activated carbon on activated carbon incorporated with calcium alginate. Adv Inorg Environ Res 6:191–198

39. Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60:309–319

40. Montgomery DC (1991) Design and analysis of experiments, 3rd edition. Wiley, New York

41. Segurola J, Allen NS, Edge M, Mahon AM (1999) Design of eutectic photo initiator blends for UV/curable acrylated printing inks and coatings. Prog Org Coat 37:23–37

42. Kim HM, Kim JG, Cho JD, Hong JW (2003) Optimization and characterization of UV-curable adhesives for optical communication by response surface methodology. Polym Test 22:899–906

43. Conley WC (1984) Computer optimization techniques. Petrocelli Books, Princeton